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TECHNICAL REPORT
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CHARACTERIZATION OF A POLYMERIC FOOD TRAY PROPOSED FOR MILITARY USE

by
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The U.S. military utilizes a wide variety of food packaging systems to deliver rations to soldiers throughout the world. Food products and packaging systems must be capable of withstanding large variations in humidity, temperature and extended storage, as well as distribution related shock and vibration. Currently, polymeric trays are being evaluated to ensure their military suitability under each of these rigorous conditions. In addition, it was necessary to determine the thermal stability, assess the thickness and the uniformity of various tray layers. The potential also exists that polymeric additives are capable of migrating from polymeric trays, thus becoming food additives. Chemical migration evaluations were conducted by way of soxhlet extractions of the polymeric tray with both 5% acetic acid and chloroform. Gas chromatography-mass spectrometry evaluation of chloroform extracts indicated the presence of aliphatic hydrocarbon oligomers from the polypropylene tray. Several antioxidants were also observed in the chloroform extracts. Analysis by differential scanning calorimetry (DSC) showed that the trays were stable at minimum and maximum temperatures. The DSC data showed that the thermal processing of the polymeric tray had a minimal effect on crystallinity. Scanning electron microscopy (SEM) revealed the quantitative thickness of the various layers.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

PREFACE

The purpose of this research was to develop and implement analytical and physical methods to evaluate the new polymeric tray food packaging system for the existence of plasticizers, antioxidants, stabilizers, processing aids, etc., to ensure that these substance are not transferred from packaging materials to food products at levels that might effect quality or present health hazards. Secondly, to determine the variabilities associated with the thickness of the tray through scanning electron microscopy and determine the thermal stability of the trays under various storage conditions.

This work was performed under Natick's Program Element AH99, Project No. 810BAF entitled "Evaluation of Chemical and Functional Properties of New Polymeric Packaging Materials."

The following registered (R) trade names are used in this report: *ACCTUF 3143* and *Amosorb* (Amoco), *Amray, J. T. Baker, Balzar, Büchi, Hewlett-Packard, Mallinckrodt, Noran, Perkin-Elmer, Polaroid, Rexan* and *Zeiss.*

This research is the first phase of the polymeric tray characterization study that was intiated on October 1, 1997.

INTRODUCTION

1. Background

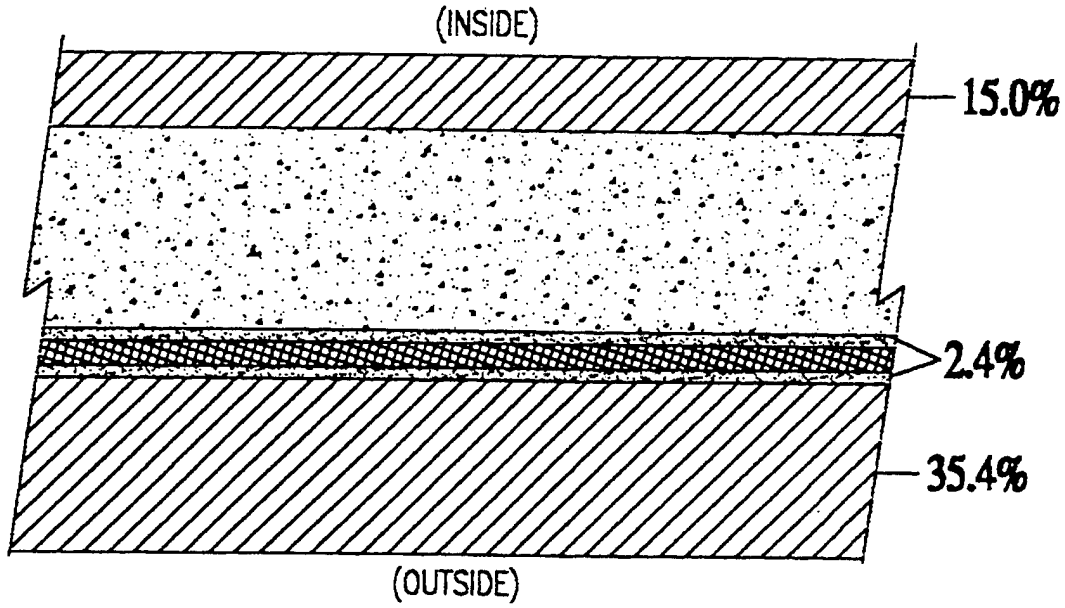
During FY96, the steel traycan used to package shelf stable heat and serve menu items for military operational rations began to show a vulnerability to internal corrosion, despite a coating designed specifically to prevent such a problem. When this corrosion occurs, food product can leak through the traycan, exposing the contents to external contaminants, and thus raising serious health and safety concerns. As a result of this internal corrosion, referred to as gray-spotting, it became necessary to identify a replacement traycan that would eliminate the performance and producibility problems associated with it, while taking maximum advantage of the latest developments in food packaging technology.

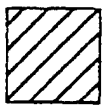
After a review and analysis [1-5] of available packaging technologies, it was concluded that a thermoformed polymeric tray was the most logical choice to replace the problem-plagued steel traycan. The commercial polymeric tray selected for full-scale testing had a weight of 125 grams, a polypropylene/ethylene vinyl alcohol/polypropylene (PP/EVOH/PP) construction, a 6 pound capacity, and a shape similar to the steel traycan. These properties make the polymeric tray inherently compatible with military operational rations currently in field use, as well as with a multitude of field food service equipment. The polymeric tray selected for testing was manufactured by *Rexam* Containers, Union, MD.

The major performance requirements for the polymeric tray include the ability to survive the rigors of military distribution (including temperatures down to -20°F), and to provide a stable food product with a shelf life of three years at 80°F or six months at 100°F. A number of technologies are being pursued to provide this extended shelf life capability for the polymeric tray including the oxygen adsorbent additive *Amosorb* [6], as well as glass surface coatings, liquid crystal polymer barrier layers and nanocomposite tray structures. *Amosorb*, an oxygen scavenger, can be blended into one or more tray layers during coextrusion, and then activated during thermal processing of the filled and sealed tray. Later during storage, *Amosorb* will adsorb permeated oxygen as well as headspace oxygen within the polymeric tray, helping to maintain food quality and extend the shelf life of the food product. To address the durability requirement, a number of design and material changes have been made to the basic commercial polymeric tray. These include constructing the tray of an improved high impact grade of polypropylene (PP), rounding the tray edges, and reinforcing the thermoformed drawn corners of the tray with additional polymer.

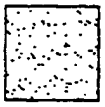
The most recent structure (Nov 97) of the polymeric container has a tray weight of 155 grams and is shown in Figure 1. The layers of this tray, from the inside to the outside, consist of: PP, recycled PP (regrind or recycled layer), a tie (or adhesive) layer, ethylene vinyl alcohol (EVOH), a tie layer, and a second layer of PP. The trays used in this study are fully described in the experimental section of this report. Retort applications usually require PP [7] or polycarbonate [8], and PP is easy to use because of cost, performance, and ease of fabrication [8]. PP is known to be brittle at low temperatures even in the amorphous state, however *Amoco's ACCTUF 3143* grade PP described herein provides sufficient flexibility for military usage. All of the polymeric trays evaluated to date have been produced in an alternative design incorporating the commercially

available oxygen scavenger *Amosorb*. This additive is typically dispersed within the tray's regrind layer as shown in Figure 1.




Polypropylene - Amoco 3143 (50.4%)


Regrind w/ 17.6% Amosorb 1000 (40%)


Adhesive (4.8%)


Evalca EVOH 'L' (4.8%)

Figure 1. The structure (Nov. 97) of the polymeric container with a tray weight of 155 grams.

All of the components described previously have been used with food packaging and are generally regarded as safe (GRAS). As a result of the manufacturing process a number of polymer additives (i.e., residual oligomers, antioxidants, plasticizers etc.) may either remain in the polymer or are added to obtain desirable effects in packaging properties [6,10]. These substances may become components of foods through migration during production, manufacture, package processing, transportation, and storage [11]. The Food and Drug Administration (FDA) requires extraction tests to measure the levels of migration [12].

Polymer additive migration may affect quality, taste, odor, or present health hazards [9,13]. Typical off-taste descriptions such as: musty, cardboardy, burnt, painty, chalky, fruity, rancid, sulfide and resinous have been blamed on polymer additive migration [13]. PP is known to develop a burnt phenolic taste from slip agents [14]. Improper drying of adhesives during the lamination process may lead to excess emissions and off-flavor [12]. Coextrusion and thermoforming at high temperatures may result in thermal degradation of the polymer, producing odors and off-taste [8]. Toxic levels have been cited in the literature [15,16], but not with any of the components described in the proposed polymeric tray.

Despite the fact that PP and the other components have been successfully used in the past, there are several factors that are unique to the military's use of the polymeric tray and these factors warrant testing of the polymeric trays:

a. Extended storage. Diffusion of polymer additives into foodstuff is a function of time. The extended storage time of military foods will result in enhanced mobility of the polymeric components. The longer the desired shelf life, the higher the temperature, the more important these residual resident levels become [8].

b. Compatibility. Food manufacturers generally select a packaging system to be compatible with the foodstuff [13]. A wide variety of fatty and non-fatty foods is targeted for the polymeric tray. The presence of fatty foods increases the extraction efficiency of the additives from the polymeric tray and will result in a larger migration of polymer additives in a shorter time.

c. Recycled plastics. Recycled plastics may have contained hazardous substances prior to recycling [17]. As the source of the recycled PP targeted for use in the tray changes, so may the hazardous nature of the additives.

d. Quality control. The use of different military contractors over the procurement lifecycle of these trays may result in different processing parameters, and we should be capable of rapidly understanding the manufacturing differences such that issues like off-taste can be rapidly determined and addressed.

e. Additives. As previously mentioned, there exists the possibility of placing the antioxidant *Amosorb* into the production polymeric tray system. While this material is considered GRAS, the presence of this additive can very well affect the other additives within the polymer by changing their mobility, diffusion and partitioning characteristics. Materials are considered GRAS only if they are used at levels no higher than necessary to perform their function (12 CFR 170.30 (h)

(1-3), 1998). The use of new additives may be limited by the amount of plasticizer already present in the PP per §178.3740 [18].

2. Factors influencing migration

While diffusional processes are quite slow in polymers [7], there are a number of processes that have been cited in an attempt to determine the mobility of packaging additives into foods. Compatibility [10], volatility [10], diffusion [10,11,19,20], partitioning [9-11,19-22], temperature [19,22], humidity [19], shock and vibration [23], component quantities [21,22], food type [24], fat content [22,24-26], contact surface area [25,26], polymer morphology [19,27], permeability [19], barrier properties [19], extractivity [10,19], thermal history [19,27], additive permanence [10], time [19], structural differences etc., are some of the many factors that influence the migration of additives into food.

Polymeric packaging, as described, has been the subject of much research into the factors influencing the migration, diffusion and partitioning of additives into the food products [7-29]. A great deal of research has been conducted to elucidate the diffusivity profiles, partitioning coefficients and related processes for the migration between polymer and foodstuff [9-11,19-22]. The amount and type of polymer antioxidant influences the mobility of additives into foodstuffs [21]. The use of antioxidants [21] such as *Amosorb* may serve to enhance the migration of polymer components through increased diffusion. The migration of components from the polymeric tray is a function of time, temperature and migration levels are highest when high fat content foods (pork, chicken etc.) are present and lowest with low-fat foods (carrots, potatoes etc.) [24]. Additive migration into triglycerides is minimal at low temperature [22] and moderate for low temperature fat-releasing foods.

In addition, higher migration rates are also observed when packaging products are subjected to vibration [23]. Printing ink and side seam lacquer migration [13,14] have been shown to occur, as have the migration of solvents used in printing and in forming the laminate on Polyester/Al/Polypropylene [26] (off flavor). Migration from slip additives used to prevent film sticking (stearamide and erucamide) [28], stearyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate in PP [23] has been observed, while the plasticizer BHT has demonstrated a higher mobility in PP than many other polymers [29].

EXPERIMENTAL

To date, a number of design iterations have taken place with the polymeric tray, many of which are reflected in the tests contained in this report. For example, the first-generation polymeric tray evaluated was a symmetric structure of PP/EVOH/PP, constructed of a standard general-purpose grade PP. These trays were produced for testing with and without the oxygen adsorbent additive *Amosorb*. Several of these earlier trays had been packed with food, thermally processed, and stored at 120°F for a period of three months before removal and emptying for initial testing, while the remainder had not been processed or stored. The newer trays had a similar symmetric structure of PP/EVOH/PP, but were constructed from *Amoco's ACCTUF 3143,* a ultra-high impact grade polypropylene (PP) resin designed to provide improved cold weather performance. The *ACCTUF 3143* trays evaluated herein had an initial tray weight of 125 grams, contained 19% PP

inside layer, 49.2% regrind with *Amosorb*, 2.4% adhesive, 6.5% EVOH, 3.9% adhesive and 19% outside PP layer for the *Amosorb* containing tray. The non-*Amosorb* containing trays had a 24.1% PP layer, 18.9% regrind layer, 1.8% adhesive, 7.6% EVOH, 3.6% adhesive and a 44% outer layer of PP. The most recent tray (Figure 1) has a 155 gram weight for both the Amosorb containing tray as well as for the non-Amosorb tray. The composition of the 155 gram tray remains consistent with Figure 1, with extra regrind PP being added if the tray is produced without *Amosorb*. This iteration of tray is currently being evaluated and the results of these evaluations are not included in this report, but are expected to be completed later this year. In addition, one of the polymer trays extracted was composed of the general-purpose grade PP tray with a 400Å glass coating (ECD - 19) covering inside surfaces.

1. Extraction

The extraction procedures were developed to establish initial levels of extractable compounds in several selected polymeric trays. A large change in the type or quantity of the compounds extracted from the polymeric tray may result in reduced food quality in the event that manufacturing processes for the trays are modified in the future. The tray pieces were extracted with chloroform to simulate the extractive behavior of fat-containing foods and with acetic acid (5%)/water (95%) to simulate the behavior of nonfat-containing foods. A series of polymeric trays were selected and extracted by Soxhlet extraction for a period of 24 hours. The 3 unretorted trays selected were: (1) the 125 gram *ACCTUF 3143* grade PP tray with no *Amosorb* or surface coatings, (2) the same PP tray with *Amosorb* incorporated into the tray, and (3) the general purpose grade PP tray with no *Amosorb*, but the inside surface coated with 400Å of SiO_x (glass). The trays without *Amosorb* were white in color while those with *Amosorb* were slightly grayer in color prior to extraction. This slight gray coloring is likely to result from the presence of the *Amosorb* dispersed within the recycle or regrind layer. Each tray was cut into approximately ½" by ½" pieces and about eight grams of the tray pieces were selected for each extraction. The exact weight of the pieces was determined prior to and after the extraction procedures.

The Soxhlet extractions were conducted with both 150 ml HPLC grade *Mallinckrodt* chloroform and with 7.5 ml of *J. T. Baker* glacial acetic acid dissolved in 142.5 ml of distilled water. All reagents were used as delivered with no further purification procedures. The chloroform extracts were reduced to a final volume of 5 ml using a *Büchi* rotoevaporator following the extraction procedure. 1µl of the chloroform solution was injected into a *Hewlett-Packard* Model 5971 gas chromatograph-mass spectrometer (GC-MS) system for analysis and identification. The GC-MS parameters included a 4 min. solvent delay to ensure that the filament would not overload and shut down the system. Therefore, any organic components with a vapor pressure equal to or less than chloroform were not detected. The GC column was a *Hewlett-Packard* HP-5, 5% phenyl methyl silicone column 30 meters in length with a diameter of .25 mm and a film thickness of .25 µ m. The linear flowrate was 33.2 cm/sec helium. The GC injection port was set at 250°C while the transfer line into the mass spectrometer was set at 250°C. The GC oven was temperature programmed to operate from 40°C with an initial time of 2-min. to a final temperature of 280°C at a ramp rate of 5°C/min. The observed mass spectrometer source operating temperature was 140°C. Injections were made with an autosampler. No GC-MS analysis was conducted on the 5% acetic

acid extracts because these materials cannot be directly analyzed by gas chromatography. Future GC-MS methods will be adapted to analyze the acetic acid/water extracts.

A GC-MS control of chloroform was prepared by following the same Soxhlet extraction procedures.

2. Scanning Electron Microscopy

Scanning electron microscopy (SEM) was performed on the various sections of the polymer tray to quantitatively determine the thickness of each of the tray layers. Samples from the 125 gram *ACCTUF 3143* grade PP tray with and without *Amosorb* were taken from the side, corner and bottom[1] areas of the tray and cut with a razor blade. Cross sections were mounted on aluminum sample stubs and coated with gold palladium (Au Pd) using a *Balzers* SCD 040 sputter coater then viewed in an *Amray* 1000Å SEM using an accelerating voltage of 10Kv. Photomicrographs were obtained using *Polaroid* Type 52 film. The thickness of each layer was determined by transferring the image from the SEM to the *Noran* TN-5500 Energy dispersive X-ray analyzer where an image processing program (IPP) was used to manually determine the thickness of each layer. Several areas of each cross section were measured and the average thickness of each layer/sample was determined.[2]

3. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was used to evaluate the glass transition temperature (T_g) as well as the melting temperature (T_m) of the polymeric tray and to determine if these transition temperatures shifted as a function of thermal annealing, storage conditions and formulations of the tray. DSC experiments were performed at 20°C/minute from –50 to 220°C using a *Perkin-Elmer* 7 instrument. Several samples in DSC pans were placed in a deep freezer for three days at –20°F while other samples were left at room temperature after undergoing storage at 120°F for 3 months.

RESULTS AND DISCUSSION

The mass of the polymeric tray pieces before and after extraction with chloroform or 5% acetic acid is shown in Table 1. The best case would occur if there were no net gain or loss of weight following the extraction procedures. However, this is rarely the case and a small mass loss of less than 5% is expected. An increase in the net mass of the pieces following extraction would have indicated that the extraction solvents had been irreversibly adsorbed or had reacted with the polymeric tray system. The mass loss observed from the polymeric trays under these extraction conditions is considered to be typical of PP. However, to ensure that none of the extracted material was either likely to result in altered taste or safety concerns the chloroform extracts were further analyzed by GC-MS.

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[1] The bottom of the tray is thermoformed with two areas of different thicknesses.

[2]The tray without the *Amosorb* appears to be constructed of 3 layers due to the consistency between the recycle and cap layers. The same tray with *Amosorb* appears to be constructed with a fourth layer which is visible due to the discoloration of the inner recycle layer by the additive itself.

Table 1. Polymeric Tray Extraction Data

Sample ID	Extraction Media	Mass before extraction (g)	Mass after extraction (g)	Percent mass retained	Percent mass lost
1. 125 g *ACCTUF 3143* grade PP tray	Chloroform	7.951	7.832	98.50	1.50
1. 125 g *ACCTUF 3143* grade PP tray	5% Acetic Acid	8.546	8.517	99.66	0.34
2. 125 g *ACCTUF 3143* grade PP tray with *Amosorb*	Chloroform	8.116	8.032	98.97	1.03
2. 125 g *ACCTUF 3143* grade PP tray with *Amosorb*	5% Acetic Acid	8.275	8.247	99.66	0.34
3. General purpose grade PP tray with 400Å glass coating (ECD - 19)	Chloroform	8.087	7.972	98.58	1.42
3. General purpose grade PP tray with 400Å glass coating (ECD - 19)	5% Acetic Acid	8.027	7.999	99.65	0.35

1. GC-MS

The GC-MS of the chloroform extracts of the 24 hour Soxhlet of all the polymeric trays indicates that most of the extractable material was hydrocarbon based oligomers from PP[3]. The presence of these oligomers in the chloroform extracts is not uncommon with PP and the maximum extraction levels of 1.5% or less are no need for great concern [30]. A comparison of Figures 2a-d shows very few significant differences between the different trays evaluated. There are groups of peaks centered around retention times of 6, 13, 20, 26, 31, 36, 40, 43, 47 and 50 minutes. The separation of these components represented various isomeric conformations of the oligomers of PP. For example, at 5 min. several configurational isomers of the oligomers with 3 repeating units were observed, at a retention time of 13 min. numerous isomers of the 4-mer (4 repeating units) were observed, at a retention time of 20 min. isomers of the 5-mer of PP were observed until the largest semi-volatile oligomers at a retention time of about 50 min., where several isomers of the 12-mer $C_{36}H_{74}$ (506 amu) were observed. This trend is likely to continue past $C_{36}H_{74}$, but larger oligomers could not be detected due to the lack of volatility of these compounds under the conditions of this analysis. This information is summarized in Table 2. Oligomers of less than 3 were too volatile to be observed by this technique while oligomers greater than 12 were too non-volatile to be observed under the conditions of this analysis.

Several additional components were also observed in the chloroform extracts of the polymeric tray. These components were additives to the PP: 2,6-di-*tert*-butyl-1,4-benzoquinone (R_t=24.48 min.), 2,4-di-*tert*-butyl-phenol (R_t=25.86 min.), 2,6-di-*tert*-butyl-4-ethyl phenol (R_t=31.77), Stearic acid (R_t=39.84), and dioctyl phthalate (R_t=46.47). None of these additives are

[3] Odorless light petroleum hydrocarbons may also be used in polypropylene, as a component of nonfood articles intended for use in contact with food per 21 CFR §178.3650.

considered a health risk at low concentrations. The 2,6-di-*tert*-butyl-4-ethyl phenol is an antioxidant designated for use with non-alcoholic foods only IAW CFR §178.2010 [18]. Since a quantitative determination was not conducted, standards will be employed in future evaluations to determine the amounts of these compounds extracted. A sample mass spectrum of 2,4-di-*tert*-butyl-phenol appears in Figure 3.

Table 2. GC-MS Data for Polymeric Tray

Approximate Retention times (min.)	Mass Observed (amu)	# of Oligomeric Repeating Units	Chemical Formula
5.28 - 6.54	128	3	C_9H_{20}
12.25 - 14.28	170	4	$C_{12}H_{26}$
19.09 - 21.12	212	5	$C_{15}H_{32}$
25.02 - 27.32	254	6	$C_{18}H_{38}$
30.33 - 31.84	296	7	$C_{21}H_{44}$
34.98 - 36.16	338	8	$C_{24}H_{50}$
39.18 - 41.06	380	9	$C_{27}H_{56}$
42.98 - 43.67	422	10	$C_{30}H_{62}$
46.47 - 47.33	464	11	$C_{33}H_{68}$
49.70 - 50.49	506	12	$C_{36}H_{74}$

In addition, it should be noted that a large number of silanated compounds were observed within the extracts from the tray with no *Amosorb* and no glass coating on the interior surface. These silanated compounds may have resulted from the extraction procedure or from surface coatings to the tray itself. The presence of these common contaminants will be carefully monitored in future extractions.

Figure 2d represents the total ion chromatogram of the solvent chloroform. A control experiment was devised by following the same extraction procedures described previously with the exception that the Soxhlet contained no polymeric material. The blank is used to determine whether any of the observed GC-MS peaks result from the extraction or analysis process. Under these conditions only small quantities of toluene, used for chloroform stabilization, were detected.

a. *ACCTUF 3143* Grade Polypropylene Tray

This tray contained no imbedded *Amosorb* or external glass coating. Extraction with the 5% acetic acid solution resulted in no warping or discoloration of the pieces. Final solutions appeared to have a slight brown color. The net loss in mass of 0.34% was highly consistent with all 3 of the polymeric trays evaluated.

Extraction with chloroform resulted in a slightly yellow cloudy solution with a precipitate of a milky white substance floating on the top. This extraction resulted in a 1.5% reduction in mass from the pieces. This was the largest mass extracted for all 3 trays. Interestingly, extraction and analysis by GC-MS of this tray indicated the presence of numerous siloxy based compounds. This

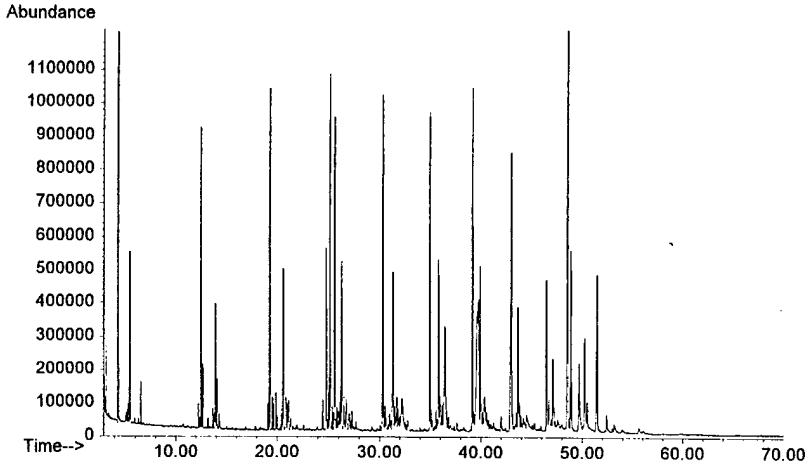

Figure 2a. Total ion chromatogram of chloroform extract of the 125g *ACCTUF 3143* grade PP tray. This tray had no *Amosorb* and no surface treatments. Predominant volatile and semi-volatile organic components are aliphatic hydrocarbons. The extractables represented 1.50% of the starting weight of the polymer.

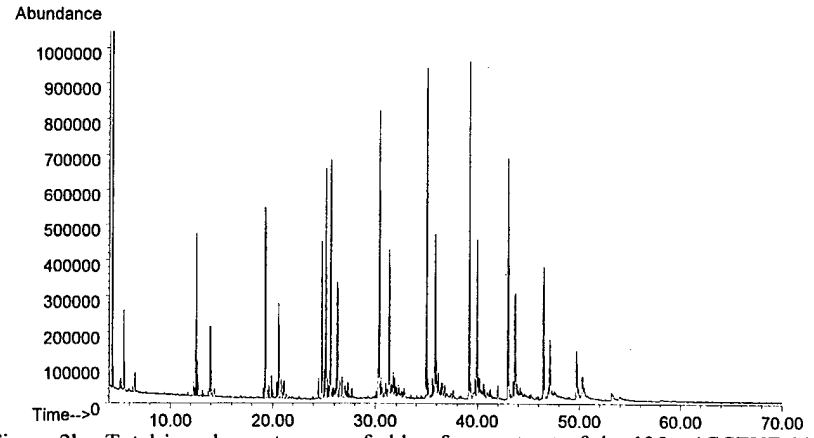

Figure 2b. Total ion chromatogram of chloroform extract of the 125g *ACCTUF 3143* grade PP tray. This tray incorporated *Amosorb* but had no surface treatments. Predominant volatile and semi-volatile organic components are aliphatic hydrocarbons. The extractables represented 1.03% of the starting weight of the polymer.

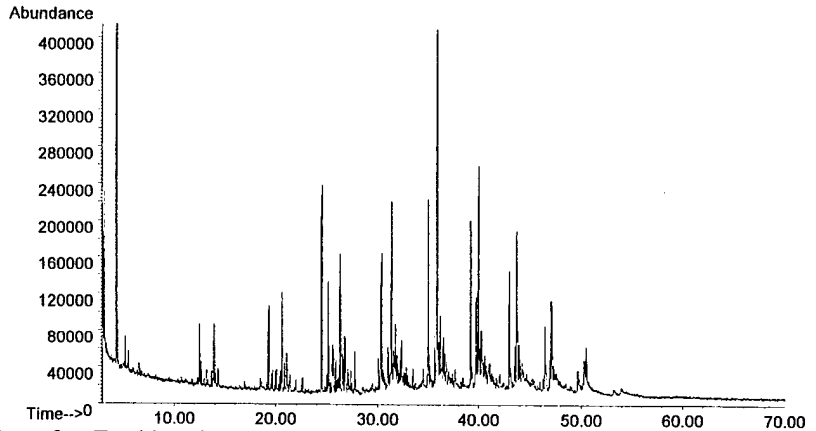

Figure 2c. Total ion chromatogram of chloroform extract of the general purpose grade PP tray (ECD-19). This tray had no *Amosorb* but the interior surface was coated with 400Å of glass. Predominant volatile and semi-volatile organic components are aliphatic hydrocarbons. The extractables represented 1.42% of the starting weight of the polymer.

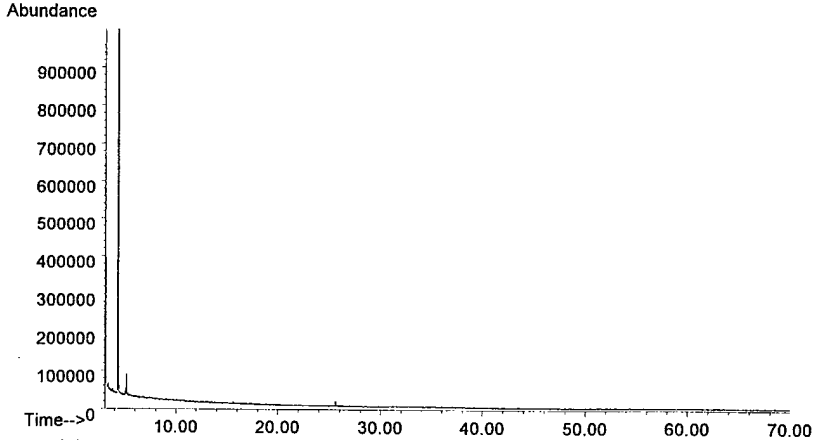

Figure 2d. Total ion chromatogram control with chloroform. The single peak represents the presence of toluene a stabilizer in the chloroform.

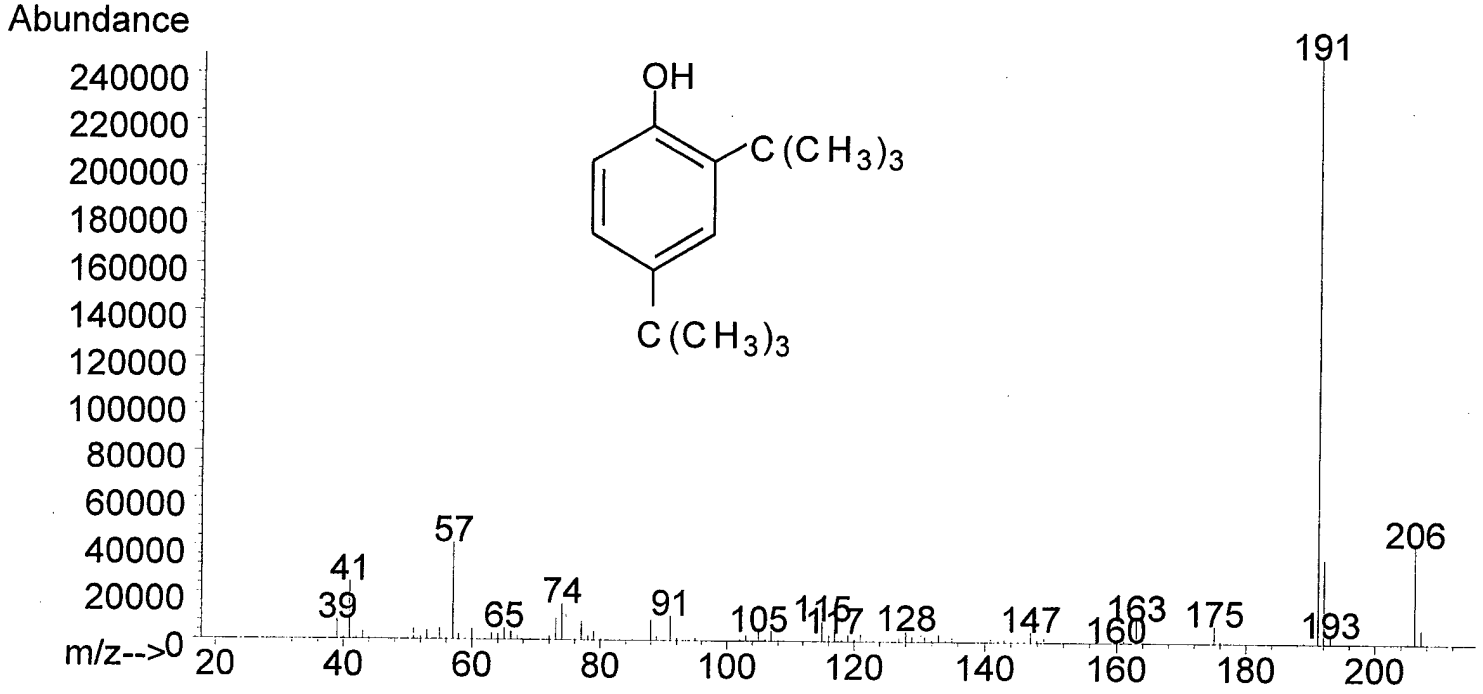

Figure 3. Mass spectrum of 2,4-di-*tert*-butyl-phenol (Rt=25.86min.). This antioxidant was observed in the chloroform extract of all 3 trays.

was remarkable only because this class of compounds was absent from the other trays. Further evaluations are necessary to determine the source of these siloxy compounds as well as their significance.

The total ion chromatogram resulting from the GC-MS analysis of the chloroform extracts is presented in Figure 2a.

b. *ACCTUF 3143* Grade Polypropylene with *Amosorb*

This tray incorporated *Amosorb* in the interior layers but did not have an external glass coating. Preliminary observations with a microscope indicated gray particles 4 to 10μm distributed within an internal layer of the tray. Following extraction with 5% acetic acid, the layer became much more visible and viewing a cross-section of this layer indicated that the particles viewed prior to extraction had now turned orange. This suggests that the *Amosorb* had a substantial amount of metallic iron present that easily oxidized to iron (II) oxide upon exposure to the hot 5% acetic acid solution. No oxidation of the *Amosorb* was observed with the chloroform extracts of the same tray. The 5% acetic acid solution had a light brown tint. Following extraction with the 5% acetic acid solution a loss of 0.35% in mass of the pieces was observed.

Exposure to the hot chloroform solutions did result in the warping of each of the individual pieces, a feature that diminished once the pieces had been thoroughly dried. The final chloroform solutions had a cloudy yellow appearance and a white milky film precipitated out across the top of the solution. Following extraction with the chloroform solution a loss of 1.03% in mass of the pieces was observed. Interestingly, the 1.03% weight loss appears to be lower than anticipated. This result shall be reevaluated in the future to determine whether this result was an anomaly or due in some way to the presence of the *Amosorb*.

The total ion chromatogram resulting from the GC-MS analysis of the chloroform extracts is presented in Figure 2b.

c. General Purpose Grade Polypropylene with Interior Coating of Glass (SiO_x)

This tray contained no imbedded *Amosorb* but had a 400Å (ECD 19) coating of SiO_x on the internal surface. It was expected that the reduced permeability of the internal surfaces resulting from the glass coating may result in reduced extractability with this tray. This was not the case as the mass reduction after extraction was 0.35% and 1.42% (5% acetic acid and chloroform, respectively) which was consistent with the mass losses observed for the other 2 tray types.

The extraction of pieces with the chloroform resulted in darker brown extract than had been observed with the other 2 polymeric trays. A milky white substance precipitated on the top of this solution. The loss in mass resulting from extraction with chloroform was 1.42%

The total ion chromatogram resulting from the GC-MS analysis of the chloroform extracts is presented in Figure 2c.

2. Scanning Electron Microscopy (SEM)

SEM samples were taken from the bottom, side and corner areas of the 125 gram *ACCTUF 3143* grade polypropylene tray with and without *Amosorb* to determine if differences existed in the thickness of the tray in these areas. Table 3 shows the thickness of each layer without the *Amosorb* while Table 4 shows the data from trays containing *Amosorb*. The tables display the average thickness measurements for the layers in each area of the tray. The range of thicknesses are also displayed to illustrate the accuracy of the total thickness. The range can be as large as 100μm and as small as 15μm. The thickness values are used as estimations as the coating process for SEM may cause some scatter in the data.

In viewing the photomicrographs (Figures 4a and 4b), one realizes how difficult it is to distinguish between the layers of the polymer tray. Photomicrographiv views of the side cuts of the tray shown in this report are representative of the other sections of the tray: the corner and the bottom of the tray. The total thickness of the samples is accurate, however the individual layer thicknesses may be somewhat subjective. The tray without *Amosorb* (Figure 4a) demonstrated three layers with the first and third layers appearing to be consistent in thickness - this most likely is PP. The inner layer (layer 2) is most likely EVOH - this layer is considerably thinner than the outer

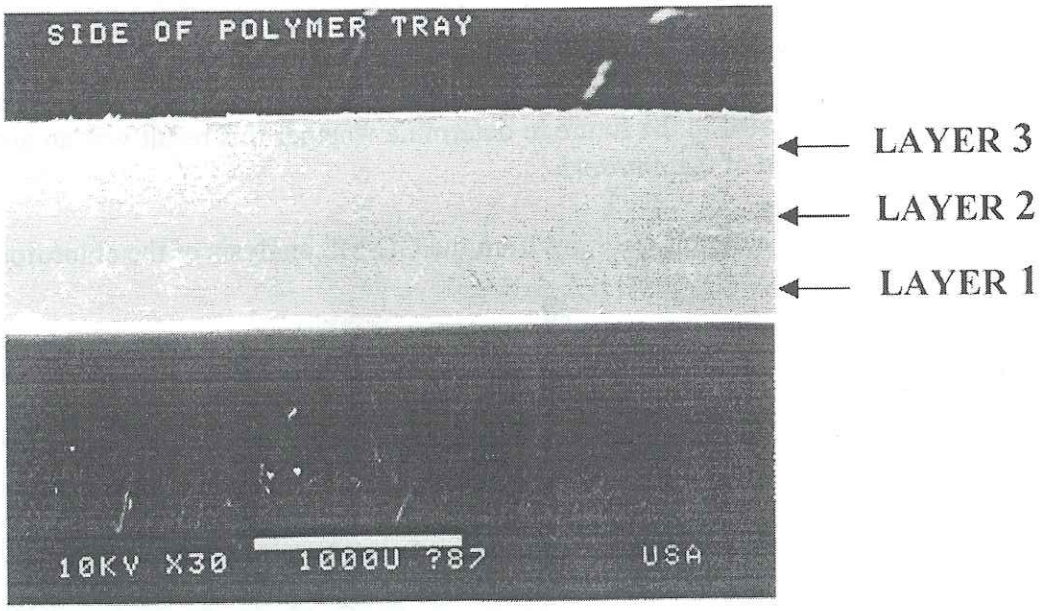

Figure 4a. Scanning electron micrograph (SEM) of the 125 gram *ACCTUF 3143* grade polypropylene tray without *Amosorb*. The thickness of various cross-sections of this tray is provided in Table 3.

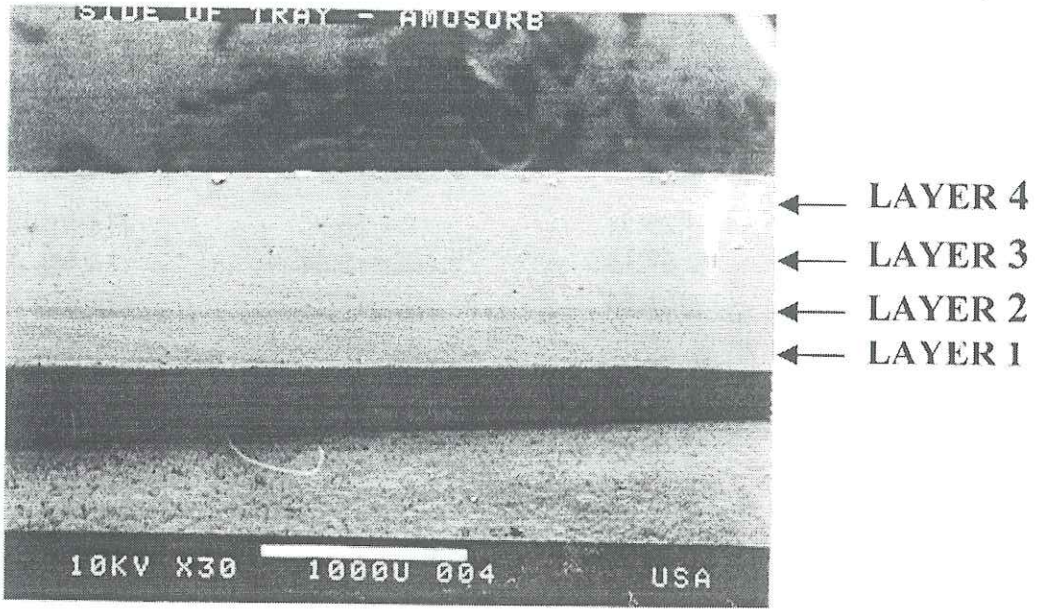

Figure 4b. Scanning electron micrograph (SEM) of the 125 gram *ACCTUF 3143* grade polypropylene tray with *Amosorb*. The thickness of various cross-sections of this tray is provided in Table 4.

layers. The tray exhibits considerable variation in its thickness from one area to another, with the bottom center (middle) portion of the tray being considerably thicker than the side and corner sections and the side of the tray being thicker than the corner portion of the tray. The reduced thickness of the layers in the corners of the tray is caused by a thinning of the polymer during the thermoforming process. Cross sections of the tray with *Amosorb* (Figure 4b) revealed that the polymer tray consisted of four layers. Here again, the first and fourth layers are fairly consistent in thickness and are most likely PP. Layer 2 (EVOH) in all instances is the thinnest layer and is very easy to distinguish in the photomicrograph. Layer 3 appears to be more porous than the other layers however, in some instances it was very difficult to distinguish where layer 3 ended and where layer 4 started. Layer 3 is the thickest layer in the cross section. This third layer maybe the reground PP and *Amosorb*. We believe it is not possible to distinguish the *Amosorb* phase by SEM. Like the tray without *Amosorb*, the center (middle) portion of the tray is the thickest portion of the tray while the corner of the tray is the thinnest. Measurements taken from an additional sample extracted from the side bottom portion of the sample reveals thicknesses just slightly thicker than the corner portion of the tray.

Table 3. SEM Measurements for Polymeric Tray Without *Amosorb*

	Average (μm)	Average (mils)	Range (μm)
SIDE OF TRAY			
Total Cross section	944.34	37.18	(918.20 - 985.40)
Individual Layers			
1st (cap)	425.51	16.75	(414.31 - 436.71)
2nd (EVOH)	67.18	2.64	(55.98 - 78.38)
3rd (cap)	451.64	17.78	(414.31 - 492.70)
CORNER OF TRAY			
Total Cross section	767.57	30.22	(739.05 - 806.24)
Individual Layers			
1st (cap)	366.49	14.43	(358.33 - 380.72)
2nd (EVOH)	26.13	1.03	(22.39 - 33.59)
3rd (cap)	371.34	14.62	(358.33 - 391.92)
BOTTOM OF TRAY			
Total Cross section	1513.58	59.59	(1433.32 - 1590.09)
Individual Layers			
1st (cap)	701.73	27.63	(649.47 - 739.05)
2nd (EVOH)	149.30	5.88	(123.17 - 156.76)
3rd (cap)	666.27	26.23	(638.27 - 705.46)

3. Differential Scanning Calorimetry (DSC)

DSC experiments were performed to evaluate the thermal stability of the trays under different conditions. The typical DSC scan (Figure 5) shows two melting peaks in the temperature range of 160-190°C, which corresponds to the melting of PP and EVOH. There is a possible overlap, however, the lower temperature and larger peak is assigned to be mostly PP. The glass transition temperature (T_g) of the EVOH is displayed as a weak step-like transition at approximately 50°C in all the scans.

Table 5 contains the literature values for the thermal transitions of EVOH and PP as well as the DSC data from a variety of trays. Note in Table 5 that tray 1 (general purpose grade PP tray with *Amosorb*) has a significantly higher enthalpy value indicating an increase in crystallinity (61.4 cal/g) when compared to tray 2 (without *Amosorb*, 51.9 cal/g) after thermal processing and storage for 3 months. All temperatures of transitions for heating remain in the range of 163 - 166 °C except for the *ACCTUF 3143* grade PP tray which is slightly higher. Repeating these experiments has shown that the thermal transitions were quite reproducible upon cycling and that there was little variation between the stored tray and the unstored general purpose grade PP tray in the thermal transitions and enthalpy values.

Table 4. SEM Measurements for Polymeric Tray With *Amosorb*

	Average (μm)	Average (mils)	Range (μm)
SIDE OF TRAY			
Total Cross section	967.01	38.07	(950.21 - 983.80)
Individual Layers			
1st (cap)	235.95	9.29	(225.55 - 239.95)
2nd (EVOH)	61.58	2.42	(52.78 - 71.98)
3rd (Reg/*Amosorb*)	494.30	19.46	(470.30 - 508.70)
4th (cap)	175.16	6.90	(153.57 - 187.16)
CORNER OF TRAY			
Total Cross section	770.24	30.32	(719.85 - 820.63)
Individual Layers			
1st (cap)	167.16	6.58	(153.57 - 182.36)
2nd (EVOH)	50.35	1.98	(43.19 - 57.58)
3rd (Reg/*Amosorb*)	407.12	16.03	(383.92 - 431.91)
4th (cap)	145.57	5.73	(124.77 - 163.16)
BOTTOM OF TRAY (MIDDLE)			
Total Cross section	1321.34	52.02	(1303.42 - 1337.01)
Individual Layers			
1st (cap)	293.38	11.55	(275.46 - 322.49)
2nd (EVOH)	87.34	3.44	(73.90 - 100.78)
3rd (Reg/*Amosorb*)	684.18	26.94	(665.15 - 705.46)
4th (cap)	254.19	10.01	(235.15 - 275.46)
BOTTOM OF TRAY (SIDE)			
Total Cross section	806.24	31.74	(777.44 - 835.03)
Individual Layers			
1st (cap)	175.16	6.90	(167.96 - 182.36)
2nd (EVOH)	47.99	1.89	(43.19 - 52.78)
3rd (Reg/*Amosorb*)	431.91	17.00	(412.71 - 446.31)
4th (cap)	154.37	6.08	(139.17 - 172.76)

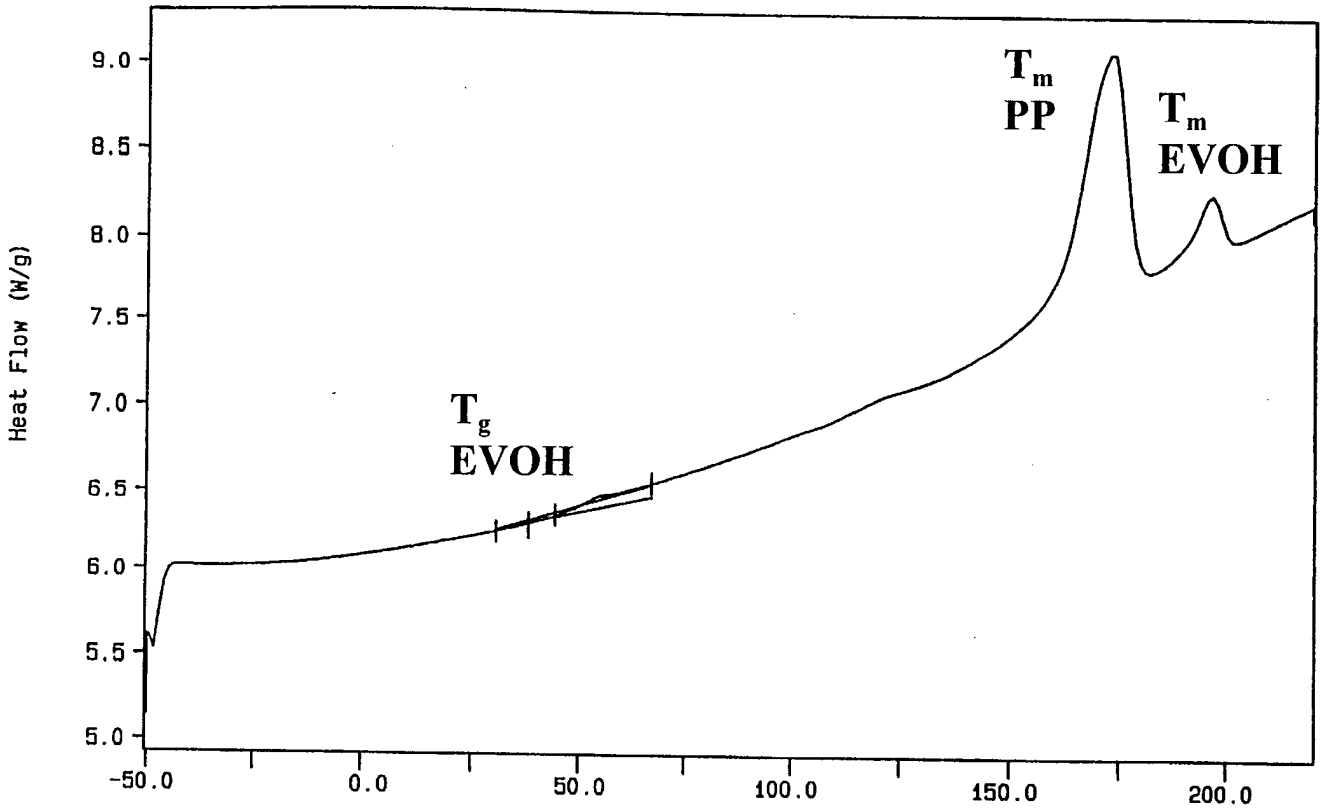

Figure 5. The differential scanning calorimetry (DSC) data of the 125 gram *ACCTUF 3143* grade polypropylene tray without *Amosorb*.

Table 5. DSC Scans of Polymeric Trays.

Literature values	T_m (°C)	T_g (°C)
EVOH	160+	42(DSC) 52(DMA)
PP	160-180	-20

Observed values	Heating		Cooling			
Tray	T(°C)	ΔH (cal/g)	T(°C)	ΔH (cal/g)	ΔH (cal/g)	ΔH
1	163	61.4	185	4.6	-73.5	-4.9
2	164	51.9	189	7.7	-59.6	-9.3
3	168	61.3	190	5.0	-71.8	-5.4
4	166	58.9	188	5.7	-72.4	-5.9

Sample: 1 = General purpose grade PP tray with *Amosorb* - stored for 3 months @120°F.
2 = General purpose grade PP tray without *Amosorb* - stored for 3 months @120°F.
3 = *ACCTUF 3143* grade PP tray without *Amosorb* - unstored.
4 = General purpose grade PP tray without *Amosorb* - unstored.

Tables 6 and 7 show samples that have been stored at -20°F for three days and at room temperature. Tray 5 (stored in freezer) and Tray 6 (stored at room temperature) have approximately the same temperature of transitions, but there is a small shift in enthalpy of the melting of PP. The sample stored in the freezer has a higher enthalpy of melting. This is also observed for the 1st heat data of tray 7 (stored at room temperature) and Tray 8 (stored in the freezer). The cool data have lower transition temperatures for the trays containing *Amosorb*. Overall, these are reproducible temperatures and enthalpy values for the trays upon thermal cycling and this again demonstrates the thermal stability of the tray.

4. Evaluation of 400Å Thick Glass Coating

Several unsuccessful attempts were made to determine the thickness and homogeneity of the SiO_x coating on one of the trays. Attempts were made to react the SiO_x surface itself and to react the polymeric substrate beneath. To date none of these efforts have been successful, but this evaluation continues as time permits. Future work will determine the feasibility of conducting the evaluation with FTIR spectroscopic techniques. This might be accomplished because the 400Å SiO_x coating may still be thin enough to allow sufficient infrared transmission to make this evaluation possible.

Table 6. DSC Data of Trays[a] Annealed at Cold (-20°F) and Room Temperatures – Heat Data.

Tray 5	Temp. (°C)	Enthalpy J/g		Temp (°C)	Enthalpy J/g
1st heat (peak1)	172.8	51.2	1st heat (peak2)	195.6	6.7
2nd heat	172.2	56.6	2nd heat	197.4	6.7
Tray 6					
1st heat (peak1)	173.8	48.2	1st heat (peak2)	197.8	7.0
2nd heat	173.7	49.3	2nd heat	197.8	7.4
Tray 7					
1st heat (peak1)	172.0	44.8	1st heat (peak2)	193.0	6.6
2nd heat	170.4	53.6	2nd heat	195.0	5.9
Tray 8					
1st heat (peak1)	170.9	49.6	1st heat (peak2)	194.5	6.4

Table 7. DSC Data of Trays[a] Annealed at Cold (-20°F) and Room Temperatures – Cool Data.

Tray 5	Temp. (°C)	Enthalpy J/g		Temp. (°C)	Enthalpy J/g
1st cool(peak1)	123.1	-61	1st cool (peak2)	169.1	-7.2
2nd cool	122.8	-61	2nd cool (peak2)	169.1	-6.8
Tray 6					
1st cool(peak1)	123.9	-64	1st cool (peak2)	170.4	-7.0
2nd cool			2nd cool (peak2)		
Tray 7					
1st cool(peak1)	117.8	-59	1st cool (peak2)	167.7	-7.6
2nd cool	116.1	-59.7	2nd cool (peak2)	168.0	-6.8
Tray 8					
1st cool(peak1)	115.4	-59.3	1st cool (peak2)	167.0	-6.9

[a]Trays 5 and 8 were stored at -20°F for 3 days while trays 6 and 7 were stored at room temperature.

CONCLUSIONS

1. The identification of organic volatile and semi-volatile components indicated that the chloroform extractable components are primarily PP oligomers. The extraction levels are much less than the maximum extraction levels cited in 21 CFR §177.1520.

2. Other additives extracted from the PP with chloroform and detected with GC-MS included: 2,6-di-*tert*-butyl-1,4-benzoquinone, 2,4-di-*tert*-butyl-phenol, 2,6-di-*tert*-butyl-4-ethyl phenol, stearic acid, and dioctyl phthalate. The concentration of these compounds and health issues related to their presence has yet to be determined.

3. Initial studies to determine the depth and homogeneity of the glass coatings have been unsuccessful, but this research is continuing.

4. The SEM shows the polymeric tray layers and gives some quantitative results for the thickness and uniformity of each layer.

5. Thermal analysis verifies that the crystallinity, glass transition temperatures, and melting temperatures are stable under a variety of cooling and heating cycling and annealing temperatures.

FUTURE WORK

1. The comparison of extraction of the various polymeric trays with chloroform will be repeated with a larger set of trays to determine whether the tray with *Amosorb* incorporated into the structure does indeed result in reduced migration of oligomeric hydrocarbons.

2. The precipitate on the surface of all the chloroform extracts will be identified and methods for quantitation will be evaluated.

3. The thickness of the glass surface may be thin enough to allow evaluation with the FTIR system. This would require several trays with differentially applied thicknesses of the glass surface. Glass generally cuts off the infrared transmission from 400 cm^{-1} to 1300 cm^{-1}. However, if this coating is thin enough it may allow FTIR evaluation of coverage and homogeneity.

4. Standards will be employed for the quantitative evaluation of additive concentrations in the polymeric tray to ensure that all indirect food additives are within FDA limits per 21 CFR §174-178.

5. SEM experiments will be performed on the latest tray iterations (155 gram/Nov 97) to quantitatively determine the layer thicknesses.

6. The thermal transitions of the various polymeric trays will be verified starting with the latest (155 gram/Nov 97) iteration, with and without *Amosorb*.

This document reports research undertaken at the U.S. Army Soldier Systems Command, Natick Research, Development and Engineering Center, and has been assigned No. NATICK/TR-98/028 in a series of reports approved for publication.

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